

Structural Characterisation of $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ($x=0.00, 0.05$ and $\text{A} = \text{Sr}$) Nano-particles Synthesised Using Combustion Technique

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(Received on: January 31, 2014)

ABSTRACT

Bismuth Ferrite (BiFeO_3) is unique among multiferroics as its ferroelectric and magnetic transition temperatures are well above room temperature. This characteristic makes them especially suitable for use in multifunctional devices such as memory devices, sensors, actuators. Various attempts have been made to prepare a solid solution of BiFeO_3 with other ions or perovskite materials by which both ferromagnetic and ferroelectric hysteresis together can be observed at room temperature for various device applications. This paper is reporting the effect of alkaline earth ion substitution on structural characteristics of the bismuth ferrite.

Keywords: Multiferroics, Bismuth ferrite, Combustion method.

INTRODUCTION

Perovskite based multiferroic materials (where more than one ferroic order co-exists) have been widely investigated due to their significance for fundamental physics and devices application [Fiebig *et al.*, 2005]. Bismuth Ferrite (BiFeO_3) is unique amongst random multiferroics as its

ferroelectric and magnetic transition temperatures are well above room temperature. BiFeO_3 ceramic has a ferroelectric-paraelectric phase transition at Curie temperature 1123K (Su *et al.*, 2011) and anti-ferroelectric-paraelectric phase transition at the Neel temperature of 643K (Wen *et al.*, 2010, Apostolova *et al.*, 2008). This characteristic makes them especially

suitable for use in multifunctional devices such as memory devices, sensors, actuators [Vaz *et al.*, 2011]. In multiferroic BiFeO₃ system, due to volatility of bismuth oxide at elevated temperature and metastability nature of the bismuth ferrite, resistivity of the material is low. This decrease in resistivity is due to formation of defects and stoichiometry of the synthesized material. So it is difficult to observe ferroelectric loop because of low resistivity of the material which results in large leakage current. Recently, there has been an increasing interest in the synthesis of multiferroics by doping alkaline ions and transition metal ions [Amit kumar *et al.*, 2011, Yongming *et al.*, 2011]. In order to resolve this problem, various attempts have been made to prepare a solid solution of BiFeO₃ with other ions or perovskite materials by which both ferromagnetic and ferroelectric hysteresis together can be observed at room temperature for various device applications [Lin *et al.*, 2008, Buscaglia *et al.*, 2006, Singh *et al.* 2008]. Perovskite structure, ABO₃ possesses high degree of structural flexibility. In perovskite structure, substitutions of various cations in the A-site produce different chemical pressure to change the B-O-B bond angle and bond distances, thereby distorting oxygen octahedral and modifying various properties of the materials having perovskite. Another way to control the volatility of bismuth oxide and stoichiometry of BiFeO₃ is to synthesize these materials using low temperature techniques.

This paper is reporting the effect of alkaline earth ion substitution on structural characteristics of the bismuth ferrite. In perovskite structure, A-site substitutions

have indirect effect to the environment of BO₆ octahedron structure. Therefore it is of interest to study the structural deformation of octahedron due to size mismatch between strontium and bismuth and hence properties of the resulting material [Ravez *et al.*, 2000; Song *et al.*, 2001]. These compositions have been prepared by novel combustion method producing nano-particles. In this synthesis technique, low temperature is used in comparison to conventional high temperature solid state reaction method, thereby minimizing the possibility of evaporation of bismuth oxide during synthesis [Glonda B. *et al.*, 2011].

EXPERIMENTAL DETAILS:

The procedure chosen for the synthesis of pure and doped bismuth ferrite nano-particles is by using novel citrate combustion method. In this method, stoichiometric ratios of starting materials, ferric nitrate (Merck), Bismuth nitrate (Merck) and nickel nitrate (SDFCL) were taken in a glass beaker and this mixture was heated on a hot plate with stirring till melting. As temperature of hot plate increased (in the temperature 100-200°C) depending on composition, auto ignition takes place and a brown colour powder (precursor) was formed. These "as prepared" powders were calcined at 950 °C for two hours. The calcined powders of each composition were mixed, grinded and pelletized using hydraulic press. These pellets were sintered in alumina crucible at 1050 °C for six hours in a high temperature furnace. The density of these sintered pellets was calculated using geometrical volume and mass. The powder x-ray diffraction patterns of the "as prepared" and sintered

pellets are obtained using RIGAKU, MINIFLEX DIFFRACTOMETER (Cu K α radiation, $2\theta = 20^\circ$ - 80°) in order to check the phase purity and calculate average crystallite size. The sintered samples were subjected to FTIR analysis for structural characterisation. To estimate the average crystalline size, the Scherer equation was used. The crystallite size (S) using the Scherer formula is given by

$$S = \frac{k\lambda}{\beta \cos \theta} \times \frac{180}{\pi}$$

where, $k = 0.9$, is a constant, depends on shape of crystal, also called shape factor, β is full width at half maximum (FWHM) of intensity versus 2θ profile, λ is wavelength of the CuK α radiation (1.54 Å), θ is the Bragg's diffraction angle.

FT-IR analysis was used to identify unknown materials, determine the quality or consistency of a sample and the amount of components in a mixture. The spectra were recorded on a Shimadzu-FTIR 8400S equipment using KBr as reference in a wave number region of 350 to 4000 cm^{-1} . The ratio of KBr and sample was taken as 95:5 in a cylindrical die and the measurement was made at room temperature.

RESULTS AND DISCUSSION

The geometrical densities for sintered pellets of pure and strontium doped bismuth ferrite are given in Table 1. Table 1 shows that the density of strontium doped sample is less than that of pure bismuth ferrite. This may be due to difference in atomic mass of strontium and bismuth atoms, formation of vacancies in doped samples and an increase in lattice parameters i.e. increase unit cell volume. Primarily it

was noticed that the volume of the unit cell increases by the increase of the lattice parameters (ionic radius). While substitution with Sr^{2+} having larger atomic radius than Bi^{3+} , enlarges the cell parameters. As a result of charge compensation, the oxygen vacancies are also created. The crystallite size calculated using Scherer formula is large for doped sample in comparison to pure bismuth ferrite sample. In doped sample, crystallite size is reduced due to formation of vacancies and deformations in lattice which hindered the grain growth during sintering.

The powder diffraction pattern of "as prepared" and sintered of pure bismuth ferrites and 5% strontium doped bismuth ferrite are given in Figures 1-4. From these patterns, it is observed that crystallinity of the samples increases after sintering. These diffraction patterns were indexed and lattice parameters were determined and given in Table 1. The lattice parameters of the strontium doped samples is more than that of pure bismuth ferrite is due to large size of substituting strontium ions in comparison substituted bismuth ions.

Table 1: Geometrical density, crystallite size and lattice parameters of pure and doped bismuth ferrite:

Composition	Density (g/cm^3)	Crystal Size (nm)	Lattice Parameters
BiFeO_3	7.5	45	$a=b=4.84$, $c=13.62\text{Å}$
$\text{Bi}_{0.95}\text{Sr}_{0.05}\text{FeO}_3$	6.0	28	$a=b=4.95$, $c=13.80\text{Å}$

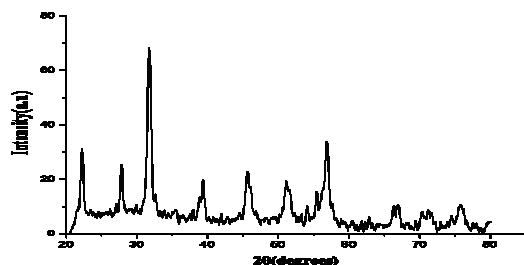


Figure 1: Powder XRD pattern of pure BiFeO_3 (as prepared) nano-particles at room temperature.

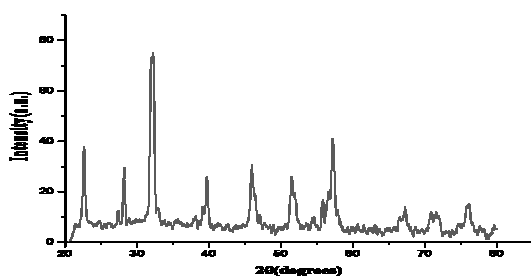


Figure 2: Powder XRD pattern of $\text{Bi}_{0.95}\text{Sr}_{0.05}\text{FeO}_3$ (as prepared) nano-particles at room temperature.

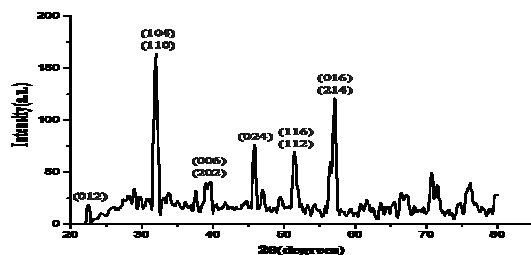


Figure 3: Powder XRD pattern of pure BiFeO_3 (sintered) nano-particles at room temperature.

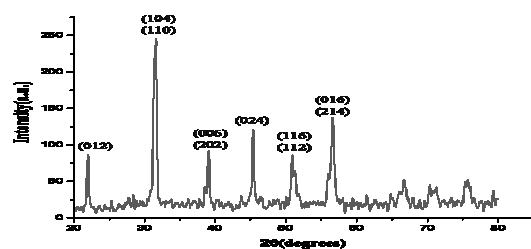


Figure 4: Powder XRD pattern of $\text{Bi}_{0.95}\text{Sr}_{0.05}\text{FeO}_3$ (sintered) nano-particles at room temperature.

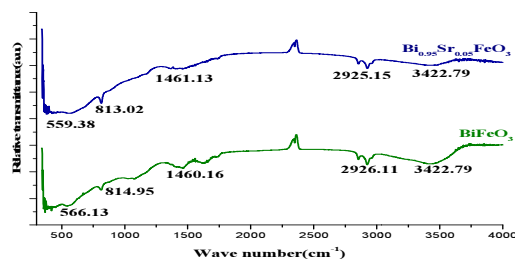


Figure 5: Comparative study of FTIR spectra of BiFeO_3 and $\text{Bi}_{0.95}\text{Sr}_{0.05}\text{FeO}_3$

The FTIR analysis of the BiFeO_3 and $\text{Bi}_{0.95}\text{Sr}_{0.05}\text{FeO}_3$ samples obtained is shown in the plots given Figure 5. The plots show a few distinct peaks. The absorption peaks at around 566cm^{-1} to 814cm^{-1} are in agreement to the study of wet chemical based synthesis of BFO as reported Y. Hu [Y. Hu *et al.*, (2011)] attribute to the Bi-O and Fe-O stretching and bending vibrations, bringing up the characteristics of the octahedral characteristic FeO_6 group in the perovskite compounds. The formation of perovskite structure can be confirmed by the presence of metal-oxygen bond. The band at around 1460cm^{-1} arose due to the presence of trapped nitrates used in synthesis. The broad band at $3000\text{--}3600\text{cm}^{-1}$ is the result of antisymmetric and symmetric stretching of H_2O and O-H bond groups.

A comparative study of the spectra of pure and doped samples show that 5% doping of strontium leads to very minute changes in the spectra. A distinct change is noticed where the doped spectra is seen to be flattened around 1461cm^{-1} . This flattening of the peaks is an event of the effect of doping that result in changes in the stretching of the metal-oxygen bonds. The peak around this region is generally the most distinct as observed in various investigations, but is

found to be missing in the obtained spectra. Moreover an extra positive peak is obtained in both the spectra at 2363cm^{-1} . This may be due to some other instrumental or analysis procedure error yet to be confirmed.

ACKNOWLEDGEMENT

Authors are thankful to department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalay for facilities. One of us (HST) is thankful to UGC, New Delhi for financial support through MRP F. No. 41–954/2012(SR).

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